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# Control of atomic layer degradation on Si substrate

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To develop 32 nm node devices, the degradation of atomic layers on the surface of Si substrates must be controlled. During the etching of a SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> hard mask or sidewall, the surface of Si is attacked due to exposure to fluorocarbon plasma. The authors have quantitatively evaluated the relationship between the energy of incident ions and the thickness of the fluorocarbon polymer for a CH<sub>2</sub>F<sub>2</sub>/CF<sub>4</sub>/Ar/O<sub>2</sub> plasma in a dual frequency CCP system. At a fixed ion energy the thickness of the damage layer ( $T_d$ ) basically depended on the thickness of the fluorocarbon polymer ( $T_{C-F}$ ). When the  $T_{C-F}$  was changed by controlling the O/CF<sub>x</sub> gas ratio,  $T_d$  had a minimum thickness under the conditions at balance point:  $P_b$ , under which the  $T_{C-F}$  was nearly equal to ion penetration depth:  $D_p$ . Using molecular dynamics simulation, reaction around the transition from SiO<sub>2</sub> to Si was clarified. The damage was done to the Si before the SiO<sub>2</sub> was completely removed, and the largest  $T_d$  was observed when the SiO<sub>2</sub> was etched off. After that,  $T_{C-F}$  began to increase because there was no longer an outflux of O from SiO<sub>2</sub> and the damage decreased as the unstable SiF<sub>x</sub> species in the damaged layer desorbed. Once the  $T_{C-F}$  became thicker than the ion penetration depth, the damaged layer got buried and  $T_d$  stopped changing. When the ion penetration depth was controlled to be equal to  $T_{C-F}$  in a steady state under low ion energy conditions, the  $T_d$  was reduced to less than 1 nm.

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## I. INTRODUCTION

Fluorocarbon plasmas have been widely used to etch dielectric materials for the fabrication of ultralarge-scale integrated circuit devices. To advance semiconductor device design, 32 nm node devices must be fabricated with an ultrashallow junction.<sup>1,2</sup> Unfortunately, the surface of Si is degraded by exposure to fluorocarbon plasma during etching of sidewalls. This unstable surface layer can cause defects or fluctuations in transistor properties because the activation of impurities doped into the source/drain region is subtly affected by the surface damage.<sup>3</sup> The minimization of substrate damage is necessary to stabilize transistor properties. Models for controlling surface reactions during etching of Si, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and SiOCH films have been extensively discussed.<sup>4-6</sup>

Steady-state etched surfaces are very sensitive to changes in radical composition as well as to ion energy. In this article, we will elucidate the relationship between the damage to Si substrates and the parameters in fluorocarbon plasma. A method of minimizing Si damage will be demonstrated.

## II. EXPERIMENTS

We used a CH<sub>2</sub>F<sub>2</sub>/CF<sub>4</sub>/Ar/O<sub>2</sub> plasma in a dual frequency CCP (60/2 MHz) system<sup>7</sup> in our experiments. The gap between the two electrodes was fixed at 35 mm. The temperatures of the top electrode, bottom electrode, and sidewall were kept at 60, 20, and 60 °C, respectively. A high-voltage probe was used to measure the peak-to-peak voltage ( $V_{p,p}$ ) of the rf-biased bottom electrode; the electron density  $N_e$  was measured with a surface wave probe. Radical densities were measured with an optical emission spectroscopy. We also used a quadrupole mass spectrometer to determine plasma

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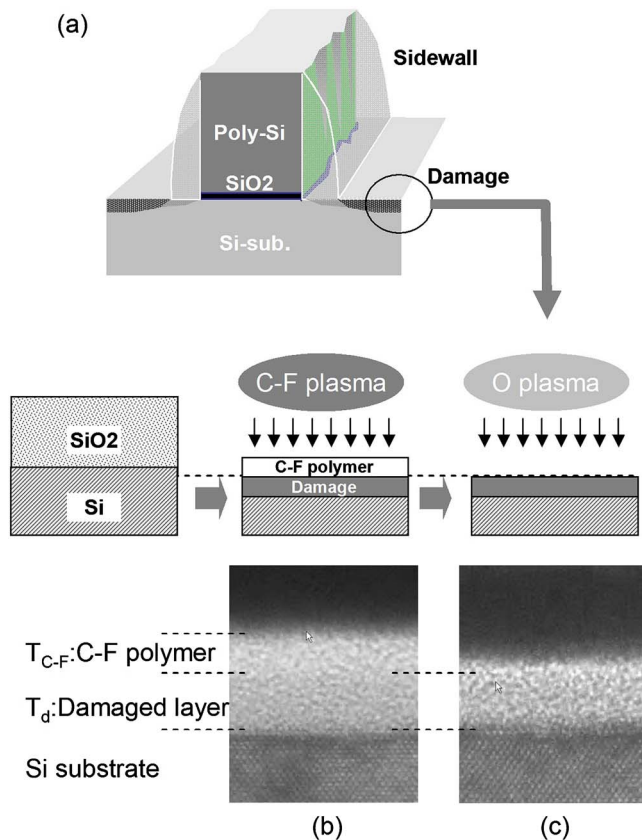


FIG. 1. Damage to Si substrate caused by exposure to  $\text{CF}_4/\text{CH}_2\text{F}_2/\text{Ar}/\text{O}_2$  plasma: (b) as etched and (c) after ashing.

potential  $V_p$ . Pressure was kept at 30 mTorr in these experiments, while partial pressure of each gas molecule in the  $\text{CH}_2\text{F}_2/\text{CF}_4/\text{Ar}/\text{O}_2$  mixture varied. The damaged layer to the Si substrate was oxidized by  $\text{O}_2$  plasma after fluorocarbon plasma irradiation. The damage thickness ( $T_d$ ) was defined by measuring the thickness of  $\text{SiO}_2$  by using ellipsometry. The thicknesses of both the damage and the C-F polymer were cross-checked using a tunneling electron microscope (TEM). Using molecular dynamics (MD) simulation,<sup>8</sup> the time dependence of the surface structure during the early stage of etching was also determined.

### III. RESULTS

#### A. Formation of degraded layer on Si substrate

We used fluorocarbon  $\text{CH}_2\text{F}_2/\text{CF}_4/\text{Ar}/\text{O}_2$  plasma to fabricate the sidewall of the transistor gate electrode [see Fig. 1(a)]. As shown by the TEM image, the top surface of the Si substrate was degraded and a fluorocarbon polymer layer was formed on the damaged layer, as shown in Fig. 1(b). We were able to remove the polymer layer using  $\text{O}_2$  ashing [Fig. 1(c)]. The damaged layer, however, remained after ashing and wet treatment. The thicknesses of the damage ( $T_d$ ) and the C-F polymer ( $T_{\text{C-F}}$ ) depended on the plasma conditions as well as the atomic compositions (especially O concentration) of etched materials.

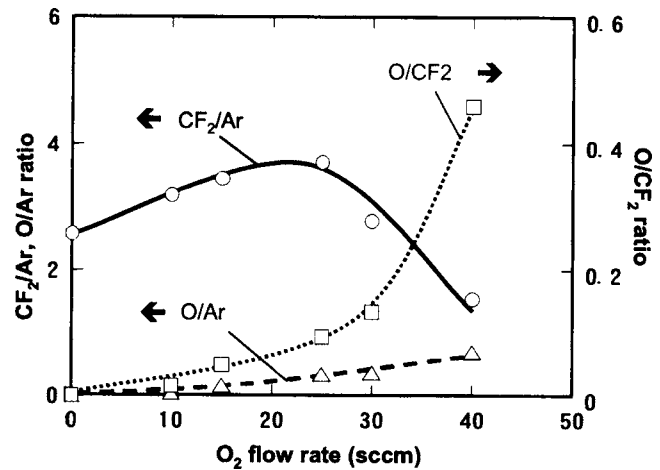


FIG. 2. Optical emission intensity ratio of  $\text{CF}_2/\text{Ar}$ ,  $\text{O}/\text{Ar}$ , and  $\text{O}/\text{CF}_2$  as a function of  $\text{O}_2$  flow rate.

#### B. Effects of radical composition on damage thickness

To clarify the relationship between the plasma conditions and the  $T_d$ , we changed the flow rate of  $\text{O}_2$  in  $\text{CH}_2\text{F}_2/\text{CF}_4/\text{Ar}/\text{O}_2$  plasma in fixed power conditions. The plasma density and  $V_{p,p}$  were  $1 \times 10^{11} \text{ cm}^{-3}$  and 1230 V, respectively. Figure 2 shows the densities of  $\text{CF}_2$  and O radicals [optical emission ratios of  $I_{\text{CF}_2}(251.8 \text{ nm})/I_{\text{Ar}}(750.4 \text{ nm})$  and  $I_{\text{O}}(777.2 \text{ nm})/I_{\text{Ar}}$ ] as a function of  $\text{O}_2$  flow rate. The ratio of O to  $\text{CF}_2$  was observed to increase monotonically with the  $\text{O}_2$  flow rate. In Fig. 3,  $T_d$  is shown as a function of the  $\text{O}/\text{CF}_2$  ratio. When we increased the  $\text{O}/\text{CF}_2$  ratio,  $T_d$  first decreased ( $\text{O}/\text{CF}_2=0-0.07$ ), then reached the minimum peak (at 0.07; condition B), and then increased again ( $>0.07$ ) though  $T_{\text{C-F}}$  decreased monotonically. Figure 4 shows  $T_d$  and  $T_{\text{C-F}}$  in conditions A, B, and C in Fig. 3 as a function of plasma exposure time. Under condition A,  $T_{\text{C-F}}$  increased linearly, indicating a constant fluo-

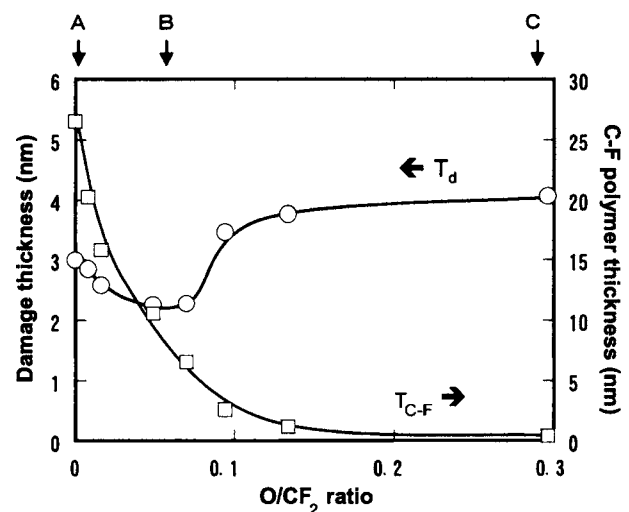


FIG. 3. Thickness of damaged layer ( $T_d$ ) and C-F polymer ( $T_{\text{C-F}}$ ) as a function of  $\text{O}/\text{CF}_2$  ratio.

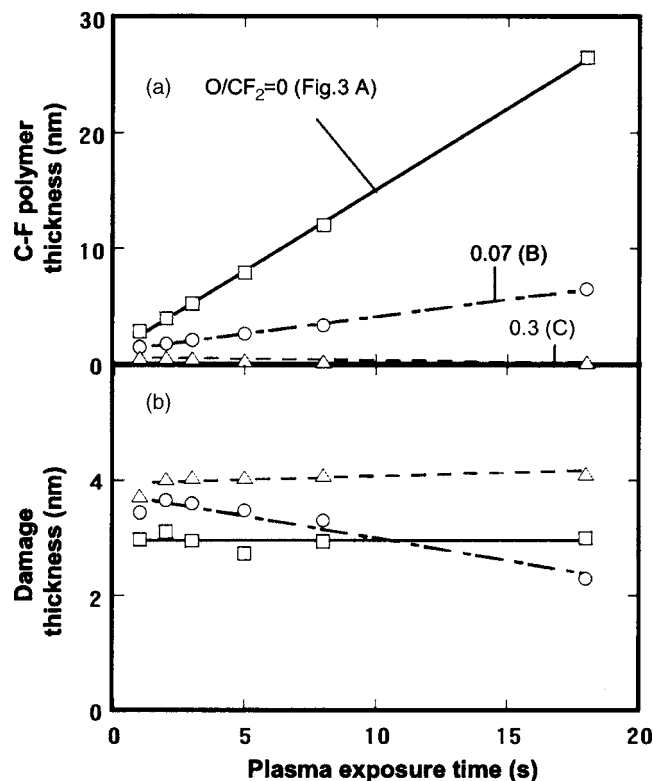


FIG. 4.  $T_d$  and  $T_{C-F}$  as a function of plasma exposure time. O/CF<sub>2</sub> ratios were 0 (A), 0.07 (B), and 0.3 (C). rf bias power was kept constant at 800 W.

rocarbon polymer deposition rate. Also under this condition, damage was done as plasma exposure began, and  $T_d$  did not change as time passed. We observed a slight decrease in  $T_d$  and a slight increase in  $T_{C-F}$  under condition B. When the O/CF<sub>2</sub> ratio was higher than B, the Si etching rate increased (condition C),  $T_{C-F}$  was thinner than 0.5 nm, and the Si was etched.  $T_d$  was relatively thick and was almost constant as time passed.

### C. Effect of ion energy on damage thickness

When we changed the substrate bias power,  $T_d$  also changed, as shown in Fig. 5.  $V_{p.p.}$  at bias powers of 1500, 800, and 400 W were 1860, 1230, and 770 V, respectively. The thicknesses of the C-F polymer were not affected by the bias power and almost the same graph (as shown in Fig. 3) was obtained for each bias condition (further decrease in ion energy, however, induced excess deposition of C-F polymer).  $T_{C-F}$  depends only on radical composition, and when we fixed the balance between the total amount of incident fluxes of CF<sub>x</sub> and O,  $T_{C-F}$  could be uniquely determined. The position of minimum peak (condition B in Fig. 3) shifted to a lower O/CF<sub>2</sub> ratio under higher bias power conditions. When the O/CF<sub>2</sub> ratio was lower than this minimum peak, we observed a deposition rate (thickness increased with time) of C-F polymer and no etching of the Si substrate.

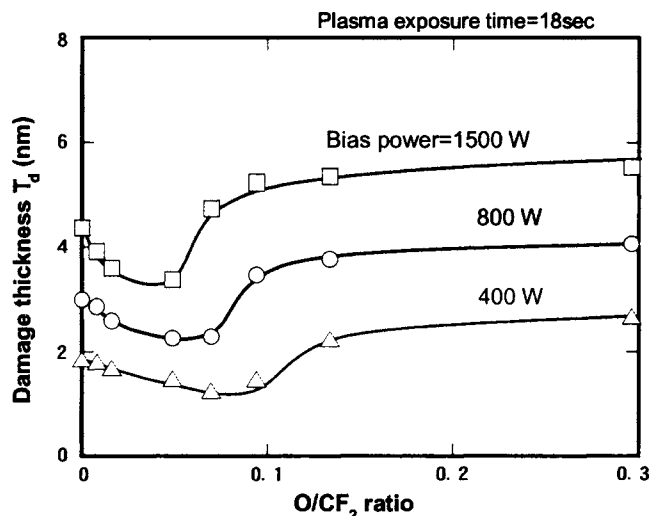


FIG. 5.  $T_d$  as a function of O/CF<sub>2</sub> ratio. Bias power was varied from 400 to 1500 W.

## IV. DISCUSSION

### A. Balance point

As shown in Figs. 3 and 5, there is a specific point where  $T_d$  has a minimum in each bias condition. We called this point the "balance point,"  $P_b$ . Since the position of  $P_b$  seemed to depend on both the ion energy and polymer thickness  $T_{C-F}$ , we quantitatively analyzed the relationship between  $T_d$  and the ion penetration depth into the C-F polymer. Figure 6(b) shows the ion energy distribution function (IEDF) calculated using the Monte Carlo simulation.<sup>9</sup> High-energy IEDF peaks at bias powers of 400, 800, and 1500 W were observed at about 780, 1230, and 1840 eV, respectively. The C-F polymer on the etched surface decelerated the ion energy during etching, showing that the amount of energy loss,  $\Delta V$ , depends on  $T_{C-F}$ . The ion penetration depth  $D_p$  was roughly estimated using data from Tatsumi *et al.*,<sup>10</sup> as shown in Fig. 6(a). For example, ions can penetrate through a 7.8-nm-thick C-F polymer at a bias power of 800 W. ( $D_p$  was experimentally obtained for ions with the averaged ion mass of all of incident ions. Therefore,  $D_p$  also depends on ion composition.) By comparing  $D_p$  in Fig. 6(a) to  $T_{C-F}$  in Fig. 7(a) (or Fig. 3), we found that  $P_b$  can be related to the point where  $T_{C-F}$  is equal to  $D_p$ . This indicated that, to minimize the damage, it is necessary to control the balance between the high-energy IEDF peak and the C-F polymer thickness on a steady-state etched surface. Next, we classify the plasma conditions into regions where  $T_{C-F}$  was thinner than  $D_p$  (Sec. IV B) and thicker than  $D_p$  (Sec. IV C) and discuss why  $T_d$  changed as radical composition and ion energy in both regions varied.

### B. Damage under "thin polymer" conditions

$T_{C-F}$  decreased monotonically as the O/CF<sub>2</sub> ratio increased. When the O/CF<sub>2</sub> ratio was larger than  $P_b$ , the Si substrate was etched and  $T_{C-F}$  was kept constant in a steady state. The ion energy deposited at the interface between the



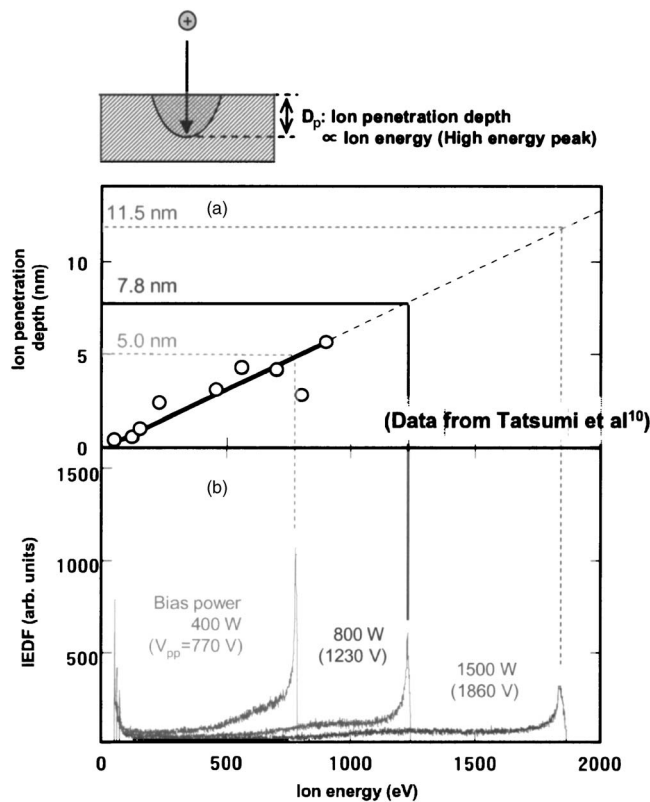


FIG. 6. (a) Penetration depth of ions (data from Ref. 10 were used) and (b) ion energy distribution.

C-F polymer and the Si substrate can be determined by both the incident ion energy (high-energy IEDF peak) and the energy consumption by the polymer (which depends on ion mass and  $T_{C-F}$ ).  $T_d$  basically depends on ion penetration depth, which is thought to depend on the net ion energy supplied below the C-F polymer, as shown in Fig. 7.  $T_d$  became thicker when incident ion energy increased or when  $T_{C-F}$  became thinner, under relatively large O/CF<sub>2</sub> conditions. To decrease  $T_d$  (and to decrease the etching rate of Si), it is necessary to decrease the O/CF<sub>2</sub> ratio under the “thin polymer” condition.

### C. Damage under “thick polymer” condition

When we used conditions where O/CF<sub>2</sub> ratio was lower than  $P_b$ , ions could not penetrate into the Si substrate in a steady state because  $T_{C-F}$  was larger than  $D_p$ . However, the degradation of the Si surface was also observed under these conditions. Furthermore,  $T_d$  became thicker when we decreased the O/CF<sub>2</sub> ratio, even though the deposition rate of the C-F polymer was relatively high. As shown in Fig. 4, this damage was formed as plasma exposure to the Si wafer began. To determine the mechanism of the formation of the degradation layer under “thick polymer” conditions, we calculated the reaction on the etched surface during the early stages of polymer formation on the Si surface using MD simulation (see Fig. 8). First, we fabricated the SiO<sub>2</sub>/Si substrate and irradiated CF<sub>3</sub> (250 eV) to form a steady-state C-F polymer during SiO<sub>2</sub> etching, as shown in Fig. 8(a).

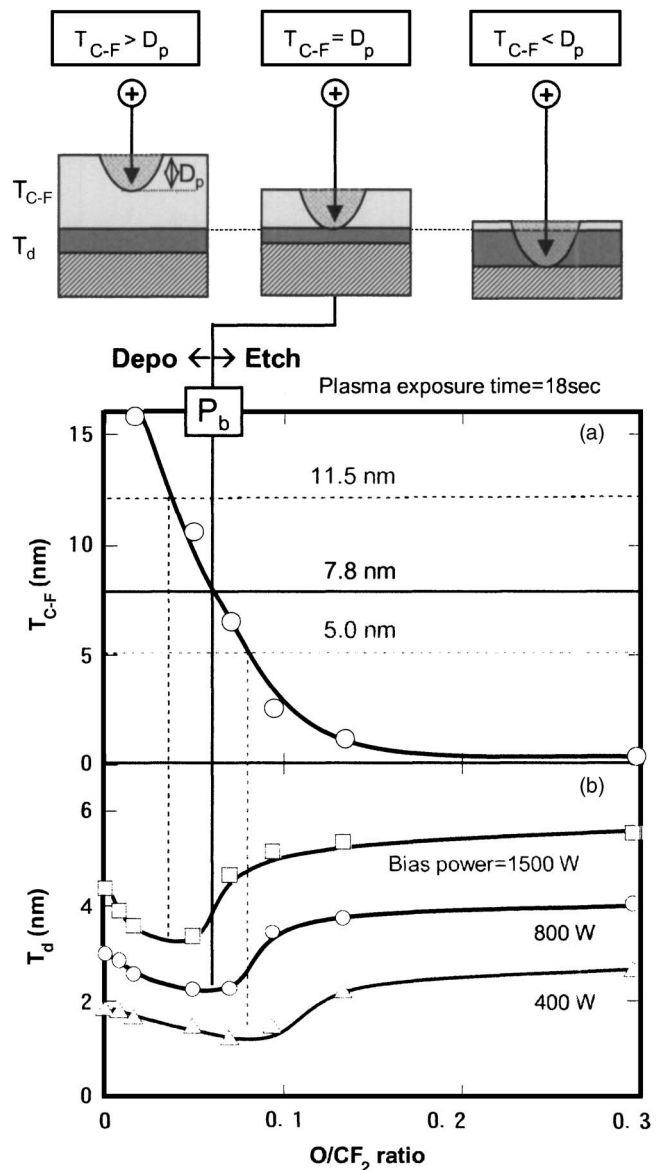


FIG. 7. (a)  $T_{C-F}$  and (b)  $T_d$  as a function of O/CF<sub>2</sub> ratio.  $T_d$  has a minimum at balance point ( $P_b$ ) where  $T_{C-F}$  was equal to ion penetration depth.

$T_{C-F}$  is relatively thin during SiO<sub>2</sub> etching. As CF<sub>3</sub> dosage on the same substrate increased, SiO<sub>2</sub> became thinner than the penetration depth of CF<sub>3</sub> and some of the CF<sub>3</sub> started to reach the underlying Si [Fig. 8(b)]. When SiO<sub>2</sub> was just etched off, the C-F polymer was still thin [Fig. 8(c)] and the degradation layer was formed on Si. When the deposition rate was relatively high, the C-F polymer started to grow thicker because C-F polymer cannot be removed by O supplied from an etched surface (Fig. 3 and A in Fig. 8). The damaged layer was covered by a thickly deposited C-F layer. On the other hand, when the polymer deposition and etching were balanced in a steady state, the damaged layer decreased slightly as dosage increased (increasing etch time), as shown in B in Fig. 8. Figure 9 shows the atomic composition of mixed layer as a function of CF<sub>3</sub> dosage. The surface composition was basically consisting of C, F, (O), and Si; and the ratios of F/C and Si/C were gradually increased along with

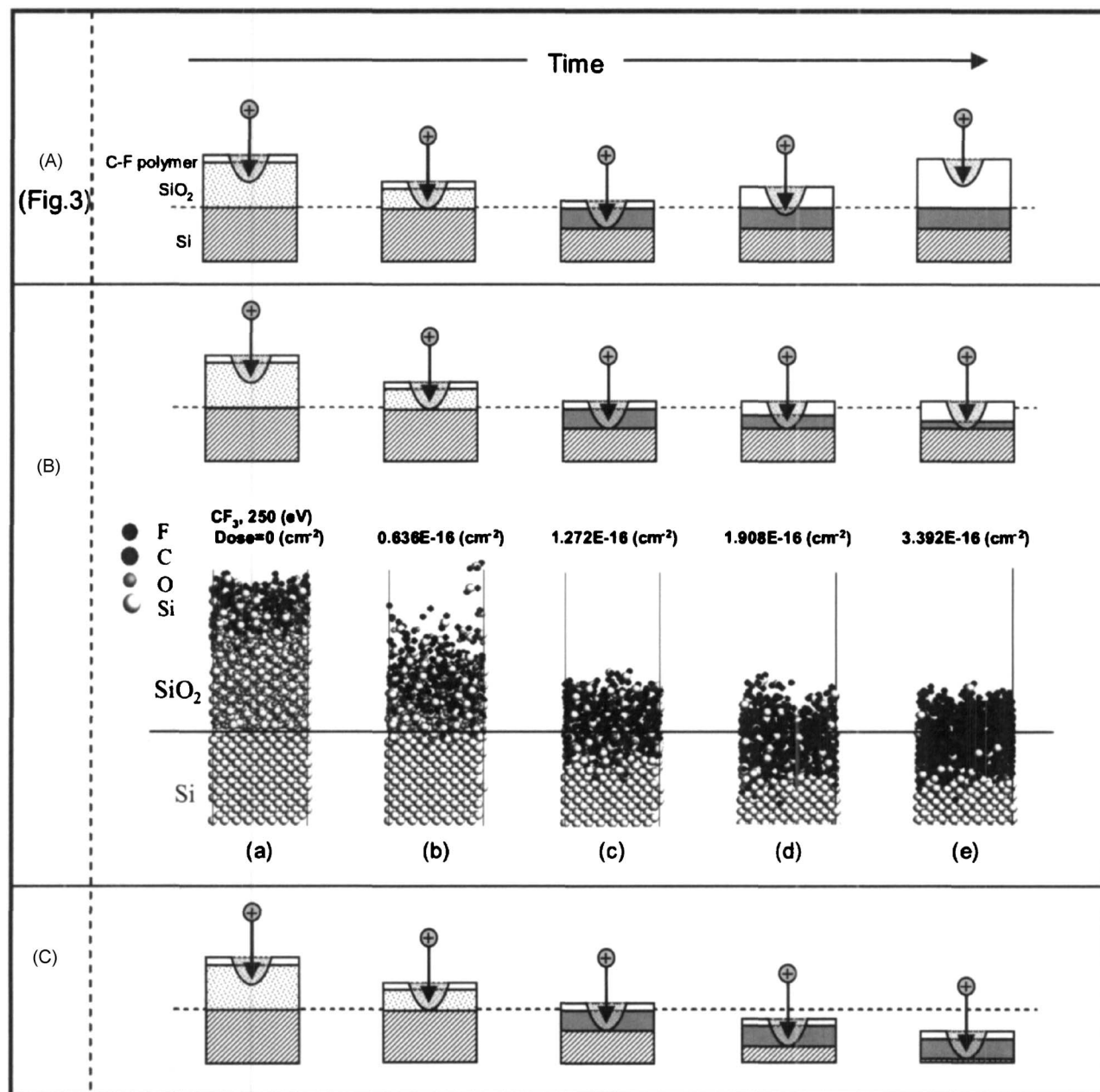


FIG. 8. Image of change in surface structure as a function of plasma exposure time. A: Thick polymer condition ( $T_{C-F} > D_p$ ). Damage [formed similarly to B (a)–(c)] was buried under polymer. B: Balance point ( $T_{C-F} = D_p$ ). Surface structure was calculated using molecular dynamics simulation.  $CF_3$  beam of 250 eV was introduced to  $SiO_2/Si$  structure. (a) During  $SiO_2$  etching. Thin polymer was formed on surface. (b) Remaining thickness of  $SiO_2$  became thinner than  $D_p$ . (c)  $SiO_2$  was etched off and damage was formed.  $T_{C-F}$  started to grow thicker. (d) Unstable C–F or Si–F species desorbed. (e) Steady-state C–F polymer was formed on a minimum amount of damage. C: Thin polymer condition ( $T_{C-F} < D_p$ ). Thinner  $T_{C-F}$  induces thicker  $T_d$ . Etching of Si also occurred.

the depth from the top surface. The interface between mixing layer and Si substrate has a F-rich composition. By increasing the dosage of  $CF_3$  injection, Si atom in mixed layer was decreased. MD calculation also suggested  $SiF_x$  was released from surface during over etching [Figs. 8(c)–8(e)]. The top part of mixing layer where Si content was low could be removed during exposure to  $O_2$  plasma [see Fig. 1(c)]. Consequently, the thinner damage was observed after longer plasma exposure under condition B. The relaxation of the degraded layer (release of unstable  $SiF_x$ ) is the reason why  $T_d$  has a minimum around  $P_b$ . As mentioned in Sec. IV B,

when steady-state  $T_{C-F}$  was thinner than  $D_p$ , the degraded layer was kept at a constant thickness, as shown in C in Fig. 8. A thinner polymer layer induces a thicker damage layer under these conditions.

Thus we have identified the mechanism of damage formation on Si. To minimize  $T_d$ , it is necessary to lower the high-energy ion peak by controlling the power and the frequency of bias power. It is also necessary to adjust the steady state of the C–F polymer so that it is the same thickness as ion penetration depth. There are many kinds of ions ( $H^+$ ,  $CH_2F^+$ ,  $CHF_2^+$ ,  $CF_3^+$ , and  $Ar^+$  were observed) and ion energy also has

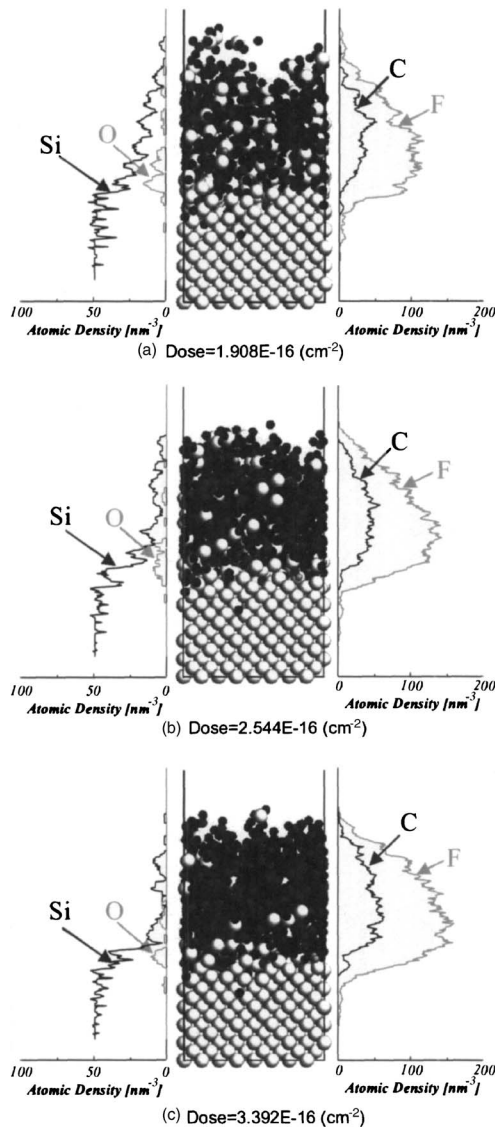


FIG. 9. Atomic composition of mixed layer (MD).  $\text{CF}_3$  dosages were (a)  $1.908 \times 10^{-16}$ , (b)  $2.544 \times 10^{-16}$ , and (c)  $3.392 \times 10^{-16} \text{ cm}^{-2}$ , respectively.

a certain dispersion, as shown in Fig. 6. The reaction is, therefore, more complex in the actual etched surface, and  $T_{\text{C-F}}$  and  $T_d$  vary depending on the etching system and gas composition used in the actual manufacturing. Quantitative monitoring and control of plasma parameters and quantitative modeling of the surface reaction will be required to minimize the fluctuation in surface damage.

## V. CONCLUSION

The mechanism of damage formation on a Si substrate during etching by fluorocarbon plasma was identified. Damage thickness  $T_d$  depends on the penetration depth of ions whose energy was decreased by a steady-state surface polymer. When the ion penetration depth was shallower than the thickness of the surface polymer, the damage was formed in the early stage of plasma exposure, when Si started to be exposed to plasma, but the polymer has not grown thicker yet. This damage was covered by the deposition of a thick C-F polymer and did not change as time exposed to plasma increased. There is an optimum point (balance point  $P_b$ ) where ion penetration depth is nearly equal to the thickness of the steady-state polymer. Under this condition, unstable bonding was released from the mixing layer of the fluorocarbon species and Si, and the thickness of the damage layer decreased. To minimize the damage, we need to quantitatively control the radical composition (thickness of C-F polymer) and ion energy (high-energy IEDF peak) to find the  $P_b$ .

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